The ethyl compound **3** reacted completely differently with but-2-yne. Instead of insertion into the Ti-Et bond, extrusion of ethene and formation of the new vinyl $Cp^*_2TiC(Me)=C(H)Me$ (**9b**) was observed. Treatment with HCl again gave **1** and *cis*-2-butene. This apparent transfer of β-H from the ethyl ligand to the substrate, i.e. but-2-yne, fits the general pattern of reactivity of titanium alkyls Cp^*_2TiR with β-H on the alkyl ligand.

Concluding Remarks. Cp^*_2TiCl is an excellent starting material for a wide range of monomeric compounds Cp^*_2TiR by reaction with alkali-metal or Grignard compounds. These paramagnetic compounds have characteristic NMR (^1H and ^2H) and EPR spectra, which can be used for identification and for monitoring their reactivity. The Ti-C bond in Cp^*_2TiR is polarized with negative charge concentrated on the ligating carbon atom. The compounds show the expected reactivity toward polar substrates when R is aryl, vinyl, benzyl, or an alkyl ligand lacking β-hydrogen. Substrates X-H with active hydrogen split off R quantitatively as RH. Unsaturated substrates, e.g. CO, CO_2, and isonitriles, insert into the Ti-C bond. When R is an alkyl ligand with β-hydrogen, the reactivity with unsaturated substrates, e.g. CO_2, alkenes, or alkynes, is dominated by extrusion of olefin R(-H).

Nonpolar substrates such as internal alkynes insert slowly into the Ti-C bond. Olefins do not insert into the Ti-C bond at all. The necessary transition state for migratory insertion is not reached in these processes. This illustrates the decreased Lewis acidity of tervalent permethyltitanocene alkyls compared with that of group 3 and lanthanide congeners and also with the cationic polymerization catalysts $[Cp^*_2MR]^+$.

Intermolecular reactions are not observed, reflecting the effectiveness of bulky Cp* ligands in the formation of reactive single-site metal centers. Paramagnetic organometallic compounds of the early transition metals have a rich and exciting chemistry, and this study demonstrates that they have so far unjustly been neglected in organometallic research.

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Supplementary Material Available: Tables of final fractional atomic and equivalent isotropic thermal parameters, anisotropic thermal parameters, and full bond lengths and angles for $Cp^*_2TiCH_2CMe_3$ (**5**) and details on experimental procedures and spectroscopic data for partially deuterated compounds Cp^*_2TiR and carboxylates $Cp^*_2Ti(\eta^2\text{-}O_2CR)$ (14 pages); a listing of observed and calculated structure factors for **5** (22 pages). Ordering information is given on any current masthead page.

(η^6-Naphthalene)(η^4-1,5-cyclooctadiene)ruthenium(0): Efficient Synthesis, Chemistry, and Catalytic Properties

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The ruthenium(0) complex (η^4-1,5-cyclooctadiene)(η^6-naphthalene)ruthenium(0), $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$ (**2**), is conveniently synthesized in 55-64% yield on a gram scale by treatment of $Ru(acac)_2(\eta^4\text{-}C_8H_{12})$ (acac = acetylacetonate) with sodium naphthalide. A preliminary ^1H NMR study of the rate of replacement of naphthalene by arenes in the presence of acetonitrile at room temperature has been made. The reaction is first order in **2** and approximately first order in acetonitrile up to $[CH_3CN]/[2]$ ca. 3, but a higher order for the latter cannot be excluded. Benzene, toluene, and xylene (8 mol per mol of **2**) in THF-d_8 replace naphthalene at almost the same rate, but the reaction is slower when there are more than two methyl groups in the entering arene, the order being *p*-xylene > 1,2,4-trimethylbenzene > 1,2,3,4-tetramethylbenzene ≫ mesitylene. The results are consistent with the initial formation of labile intermediate η^4- or η^2-naphthalene complexes that are stabilized by acetonitrile, e.g., $Ru(\eta^4\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})(NCMe)$. Solutions of **2** in acetonitrile lose naphthalene to form a dinuclear μ-naphthalene complex $Ru_2(\eta^4\text{-}C_8H_{12})_2(\mu\text{-}C_{10}H_8)$ (**5**). The new η^6-arene complexes $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})$ (arene = C_6H_5CN (**4**), 1,2,4-$C_6H_3Me_3$ (**6**), 1,2,3,4-$C_6H_2Me_4$ (**7**), $C_6H_5CH=CH_2$ (**9**), 1-Me-4-CH_2=$CMeC_6H_4$ (**10**), (*E*)-$C_6H_5CH=CHC_6H_5$ (**11**), $(C_6H_5)_3As$ (**14**), and $(2\text{-}MeC_6H_4)_3P$ (**15**) have been obtained from **2**, and the new ruthenium(II) complexes $[RuCl_2(\eta^6\text{-arene})]_2$ (**12**) and $Ru(O_2CMe)_2(\eta^6\text{-arene})$ (**13**) (arene = 1-Me-4-CH_2=$CMeC_6H_4$) have been prepared from **10**. Protonation of **2** with HPF_6 gives the hydridoruthenium(II) complex $[RuH(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})]PF_6$ (**16**), from which naphthalene is readily displaced by *p*-xylene or mesitylene to give $[RuH(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})]PF_6$. In the presence of acetonitrile and hydrogen (1-20 atm), **2** catalyzes the hydrogenation of olefins. It is much more active than $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})$ (arene = C_6H_6, 1-Me-4-$Me_2CHC_6H_4$) under the same conditions, probably as a consequence of the ease of $\eta^6 \rightarrow \eta^4$ conversion for naphthalene.

Introduction

It is now well-established that η^5-indenyl complexes undergo substitution reactions more readily than corresponding η^5-cyclopentadienyl complexes, probably as a consequence of the stabilization of a η^3-indenyl transition state or intermediate.[1] A similar effect probably operates

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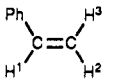
Table I. Analytical and Spectroscopic Data for New Ru(η^6-arene)(η^4-C_8H_{12}) Complexes

complex	anal. %C calcd (found)	anal. %H calcd (found)	MS, m/z[a]	^{1}H NMR, δ (C_6D_6) η^6-arene	^{1}H NMR, δ (C_6D_6) η^4-C_8H_{12}
Ru(η^6-C_6H_5CN)-(η^4-C_8H_{12}) (**4**)[b,c]	57.7 (57.9)	5.5 (5.7)	313	5.10 (t, 1 H), 5.60 (t, 2 H), 5.72 (d, 1 H)	3.56 (br s, 4 H, =CH), 2.2–2.05 (m, 8 H, CH_2)
Ru(η^6-1,2,4-$C_6H_3Me_3$)-(η^4-C_8H_{12}) (**6**)	62.0 (61.8)	7.3 (7.65)	330	4.72–4.60 (unsym 5-line pattern, 3 H, C_6H_3), 1.72 (s), 1.67 (s), 1.64 (s) (each s, 3 H, Me)	3.06 (m, 4 H, =CH), 2.36 (m, 8 H, CH_2)
Ru(η^6-1,2,3,4-$C_6H_2Me_4$)-(η^4-C_8H_{12}) (**7**)	62.9 (62.0)	7.6 (8.05)	344	4.71 (s, 2 H, C_6H_2), 1.71, 1.63 (each s, 6 H, Me)	2.91 (m, 4 H, =CH), 2.35 (m, 8 H, CH_2)
Ru(η^6-C_6H_5CH=CH_2)-(η^4-C_8H_{12}) (**9**)[d]	61.3 (61.4)	6.4 (6.7)	290	6.09 (dd, 1 H, H^1), 5.18 (dd, 1 H, H^3), 4.97 (dd, 1 H, H^2, CH=CH_2, J_{12} = 10.8 Hz, J_{13} = 16.4 Hz, J_{23} = 1.0 Hz), 4.96–4.77 (m, 6 H, C_6H_5)	3.42 (br s, 4 H, =CH), 2.33 (m, 8 H, CH_2)
Ru(η^6-1-Me-4-CH_2=$CMeC_6H_4$)(η^4-C_8H_{12}) (**10**)	63.3 (63.1)	7.0 (7.4)	341	5.07 (s), 4.92 (m) (each 1 H, =CH_2), 4.91, 4.61 (ABq, 4H, C_6H_4, J = 5.6 Hz), 1.99, 1.84 (each s, 3 H, MeC=C, C_6H_4*Me*)	3.25 (br s, 4 H, =CH), 2.31 (br s, 8 H, CH_2)
Ru(η^6-*trans*-PhCH=CHPh)(η^4-C_8H_{12}) (**11**)	67.8 (67.5)	6.2 (6.2)	390	7.4–7.0 (m, 5 H, C_6H_5 uncoord), 6.63, 6.57 (AB q, 2 H, CH=CH, J = 16 Hz), 5.06 (d, 2 H, J = 5.4 Hz), 4.92 (t, 1H, J = 5.4 Hz), 4.84 (t, 2 H, J = 5.4 Hz, C_6H_5 coord)	3.48 (m, 4H, =CH), 2.31 (m, 8H, CH_2)
Ru(η^6-$C_6H_5AsPh_2$)-(η^4-C_8H_{12}) (**14**)	60.6 (60.9)	5.3 (5.6)	516	7.58–7.52 (m, 4 H), 7.13–7.05 (m, 6 H, C_6H_5 uncoord), 5.27 (tt, 1 H), 4.67 (dt, 2 H), 4.46 (complex t, 2 H, C_6H_5 coord)	3.56 (m, 4 H, =CH), 2.44–2.26 (m, 8 H, CH_2)
Ru[η^6-2-MeC_6H_4P-(C_6H_4Me-2)$_2$](η^4-C_8H_{12})[e] (**15**)	*f*	*f*	514	7.3–6.8 (m, 8 H, C_6H_4 uncoord), 5.45 (td, 1 H), 4.73 (d, 1 H, J = 5.6 Hz), 4.63 (m, 1 H), 4.11 (td, 1 H, C_6H_4 coord), 3.01 (s, 3 H), 2.40 (d, 3 H, J_{PH} = 1.4 Hz), 1.76 (d, 3 H, J_{PH} = 1.2 Hz)(Me)	3.32 (m, 4 H, =CH), 2.41–2.20 (m, 8 H, CH_2)

[a] Mass of most intense peak in cluster due to parent ion. [b] ^{1}H NMR in CD_2Cl_2. [c] $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 89.13, 89.00, 81.03 (Ar C), 65.29 (=CH), 33.46 (CH_2). [d] Proton numbering:



[e] $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6) δ −36.5 (s); singlet at δ −30.3 of about equal intensity due to free P(*o*-tolyl)$_3$ and singlets due to small amounts of unidentified species at δ −41.7, −42.7 also observed. [f] Insufficient sample for elemental analysis.

in η^6-naphthalene ($C_{10}H_8$) complexes, especially those of the group 6 metals. For example, the coordinated arene is more easily displaced by ligands such as CO or tertiary phosphines from Cr(η^6-$C_{10}H_8$)(CO)$_3$ or Cr(η^6-$C_{10}H_8$)$_2$ than from Cr(η^6-C_6H_6)(CO)$_3$ or Cr(η^6-C_6H_6)$_2$.[2-7] Extended Hückel calculations on Cr(η^6-$C_{10}H_8$)(CO)$_3$ have shown that it requires about 24 kcal/mol to attain the most stable η^2 geometry, whereas the corresponding value for Cr(η^6-C_6H_6)(CO)$_3$ is about 35 kcal/mol.[8]

In 1984 Vitulli and co-workers[9] reported that (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium(0), Ru(η^6-C_8H_{10})(η^4-C_8H_{12}) (**1**), reacts with naphthalene under hydrogen to give the η^6-naphthalene complex Ru(η^6-$C_{10}H_8$)(η^4-C_8H_{12}) (**2**) in 80% yield. They showed that the coordinated arene in **2** is more labile than those in other Ru(η^6-arene)(η^4-C_8H_{12}) complexes, being easily replaced by other arenes at room temperature in the presence of acetonitrile; the resulting Ru(η^6-arene)(η^4-C_8H_{12}) complexes are then easily converted into ruthenium(II) compounds [$RuCl_2$(η^6-arene)]$_2$ by the action of HCl.[10,11] These important precursors are often conveniently prepared in gram quantities by the dehydrogenation of 1,3- or 1,4-cyclohexadienes with ethanolic $RuCl_3$,[12] but this method cannot be used if there are substituents in the arene ring that do not withstand the reducing conditions required to prepare the dihydroarene. Syntheses based on **1** or **2** circumvent this difficulty but at present they suffer from the disadvantage that the high yields reported for **1** and **2** (ca. 80%) refer to quantities of $RuCl_3$ of less than 1 g, and, in our experience, larger scale reactions can give poorer yields.

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A recent paper, which fails to acknowledge the earlier work of Vitulli et al.,[9] reports that **2** can be prepared in 10–20% yield from the reaction of $[RuCl_2(\eta^4\text{-}1,5\text{-}C_8H_{12})]_n$ with lithium naphthalide ($LiC_{10}H_8$) in THF and also describes the X-ray crystal structure of **2**.[13] We have independently made **2** by a similar method[14] and have also determined the structure of the compound.[15] Since our structural results are identical with those of ref 13, within experimental error, we shall restrict our attention in this report to a better synthesis of **2** and to an investigation of some of its chemistry and catalytic properties.

Experimental Section

All operations were performed under argon with use of standard Schlenk techniques. Solvents were distilled before use from the drying agent in parentheses: tetrahydrofuran (sodium/benzophenone), THF-d_8, benzene-d_6, mesitylene, 1,2,4-trimethylbenzene and 1,2,3,4-tetramethylbenzene (sodium), and acetonitrile and benzonitrile (CaH_2). Acetone was either distilled or dried over 4A molecular sieves. 1-Hexene was distilled before use and stored under argon. NMR (^1H, ^{13}C) spectra were recorded on Jeol FX200, Varian XL200, or Varian Gemini 300 instruments, IR spectra on a Perkin-Elmer 683 spectrometer, and mass spectra at 70 eV on a VG Micromass 7070 instrument. Elemental analyses were carried out in the Microanalytical Laboratory of the Research School of Chemistry, ANU, Canberra, Australia. VPC analyses were done on a Perkin-Elmer 8500 gas chromatograph equipped with a 12 m × 0.22 mm BP1 capillary column; the carrier gas was helium. Elemental analyses and spectroscopic data for new $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})$ complexes are collected in Table I.

p-Isopropenyltoluene was prepared either by the action of methylmagnesium iodide on ethyl *p*-toluate and subsequent dehydration of the resulting *p*-tolyldimethylcarbinol with $KHSO_4$,[16] or by the action of $Ph_3P^+\text{–}CH_2^-$ on methyl *p*-tolyl ketone. The complexes $[RuCl_2(\eta^4\text{-}1,5\text{-}C_8H_{12})]_n$[17] and $Ru(acac)_2(\eta^4\text{-}1,5\text{-}C_8H_{12})$[18] were prepared by literature methods.

Preparation of $Ru(C_{10}H_8)(C_8H_{12})$ (2). A solution of sodium naphthalide, prepared from naphthalene (1.57 g, 12 mmol) and freshly cut sodium (1.12 g, 44 mmol) in THF (50 mL) over 2 h, was added dropwise to a solution of $Ru(acac)_2(C_8H_{12})$ (2.0 g, 4.9 mmol) in THF (60 mL), which was stirred magnetically and cooled in dry ice/acetone. The wine-red solution was stirred for 3 h at −78 °C and then allowed to come to room temperature overnight with continued stirring. The volume of the solution was reduced to ca. 20 mL under reduced pressure and the brown suspension was siphoned under argon onto a column of alumina (neutral, activity III, approximately 6 cm long and 4 cm in diameter) covered with sand and cooled in ice. Elution with THF gave an orange-brown solution (ca. 200 mL), which was evaporated to dryness. Naphthalene was removed from the residual solid by sublimation at ca. 20 °C (10^{-5} mm) on to a probe cooled to −20 °C; 80–90% of the theoretical amount was recovered. The solid was dissolved in THF (15 mL) and the filtered solution was treated with hexane (50 mL). The mixture deposited brown crystals of **2** after being kept at −78 °C overnight. These were washed with hexane (2 × 10 mL) at −60 °C and dried in a vacuum. The yield of **2** was 0.90–1.05 g (55–64%). ^1H NMR (C_6D_6) δ 7.11 (s, uncoord ring, 4 H, $C_{10}H_8$), 5.60, 4.29 (AA′BB′), 4 H, coord ring, $C_{10}H_8$), 3.58 (s, 4 H, =CH), 2.00 (br s, 8 H, CH_2); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 127.2, 126.3 (uncoord ring, $C_{10}H_8$), 106.1 (ring junction, $C_{10}H_8$), 91.3, 74.5 (coord ring, $C_{10}H_8$), 63.5 (=CH), 33.2 (CH_2); mass spectrum, *m/z* (quoted mass numbers refer to the most intense peak, corresponding to ^{102}Ru, of a cluster of peaks) 338 (M^+), 308, 230 ($M^+ - C_8H_{12}$), 206, 128 ($C_{10}H_8$); IR (cm^{-1}, KBr) 2960 m, 2910 m, 2850 m, 2800 m, 1480 w, 1435 w, 1360 w, 1315 m, 1243 w, 1230 m, 1195 w, 1150 w, 1005 w, 992 w, 953 w, 905 w, 865 m, 820 m, 770 w, 745 ms, 620 w, 515 w, 490 w, 480 m, 385 w, 325 w, 310 w. Anal. Calcd for $C_{18}H_{20}Ru$: C, 64.1; H, 6.0. Found: C, 63.9; H, 6.2.

Preparation of $Ru_2(C_8H_{12})_2(\mu\text{-}C_{10}H_8)$ (5). A sample of **2** (15 mg, 0.044 mmol) was placed in a 5-mm NMR tube, which was then closed with a suba seal fitted with a needle supplying argon or vacuum. Acetone (1.5 mL) was added from a syringe and the tube was shaken until all the solid had dissolved. While the tube was kept very still, acetonitrile (32 μL, 0.61 mmol) was carefully added dropwise to form two layers of liquid. At the boundary the solution was red and over several hours long red-brown needles grew. The liquid was carefully removed by syringe, taking care not to dislodge the crystals from the sides of the tube. The last traces of solvent were removed in a vacuum and the crystals of **5** were carefully removed from the sides of the tube; this can be done in air in which the crystals are stable for at least 15 min. The preparation can be carried out on a larger scale in a Schlenk flask, using **2** (50 mg, 0.74 mmol), acetone (5 mL), and acetonitrile (39 μL). After 1 h the product precipitates as a red powder of poorer quality than that grown slowly in an NMR tube. ^1H NMR (C_6D_6) δ 5.45, 4.01 (AA′BB′, each 4 H, $C_{10}H_8$), 3.56 (m, 8 H, =CH), 2.01 (m, 16 H, CH_2); mass spectrum, *m/z* 548 (M^+), 338. Anal. Calcd for $C_{26}H_{32}Ru$: C, 57.1; H, 5.9; N, 0.0. Found: C, 56.8: H, 6.0; N. 0.0.

Protonation of $Ru(C_{10}H_8)(C_8H_{12})$ (2). A filtered solution of **2** (400 mg, 1.18 mmol) in ether (60 mL) was cooled in ice, stirred well, and treated with 4–6 drops of 65% aqueous HPF_6 to give a pale yellow solid. After 1 h, the supernatant liquid was removed by decantation and the residual solid was dried in vacuo. Addition of more HPF_6 to the yellow-brown supernatant gave more pale yellow solid, which was isolated similarly. The total yield of $[RuH(C_{10}H_8)(C_8H_{12})]PF_6$ (**16**) was 450 mg (79%). ^1H NMR (CD_2Cl_2) δ 7.90 (complex d, uncoord ring, $C_{10}H_8$), 6.33 (s, coord ring, $C_{10}H_8$), 4.31 (m), 3.95 (m) (=CH), 2.30 (m), 1.84 (approx d), 1.61 (approx d), 1.31 (m) (CH_2), −6.73 (RuH); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 133.7, 128.4 (uncoord ring, $C_{10}H_8$), 126.4 (ring junction, $C_{10}H_8$), 93.5, 92.5 (coord ring, $C_{10}H_8$), 80.2, 74.9 (=CH), 31.5, 28.9 (CH_2); IR (cm^{-1}, Nujol) 2050 w [ν(RuH)], 865 s, 840 vs, 560 s (PF_6).

Preparation of (η⁶-Benzonitrile)(η⁴-1,5-cyclooctadiene)ruthenium(0), $Ru(\eta^6\text{-}C_6H_5CN)(\eta^4\text{-}C_8H_{12})$ (4). Benzonitrile (0.29 mL, 2.85 mmol) was added to a solution of **2** (160 mg, 0.075 mmol) in THF (40 mL) and the mixture was set aside at room temperature for 2 days. The brown solution was evaporated to dryness under reduced pressure and naphthalene was removed by sublimation at 10^{-5} mm on to a −30 °C probe. The residue was dissolved in hexane and chromatographed on neutral alumina (grade III). The eluate was concentrated to ca. 10 mL and set aside overnight in a dry-ice bath. After filtration, air-stable yellow crystals of **4** (74 mg, 52%) were obtained. IR (cm^{-1}, KBr) 2220 [ν(CN)].

Replacement of Naphthalene in 2 by Other Arenes. General Procedure. Known amounts of **2** and the arene in a tube or Schlenk flask fitted with a magnetic stirring bar and serum cap were treated with solvent (if the arene was not liquid) and acetonitrile. The vessel was either sealed or kept under argon and the mixture was stirred until reaction was judged to be complete. The mixture was evaporated to dryness and naphthalene was removed as described above. The solid was dissolved in ether or THF and chromatographed on neutral alumina (grade III). The product eluted with ether/hexane or benzene/hexane and, after removal of solvent under reduced pressure, was usually pure as judged by ^1H NMR spectroscopy. It could be recrystallized from hexane or isopentane. Reaction conditions and product yields are summarized in Table II.

Reaction of $Ru(\eta^6\text{-}1\text{-}Me\text{-}4\text{-}CH_2{=}CMeC_6H_4)(\eta^4\text{-}C_8H_{12})$ (10) with HCl. Complex **10** (150 mg) was dissolved in acetone (50 mL) and concentrated HCl (0.25 mL) was added dropwise with stirring. The color changed from yellow to red-brown. After 30

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Table II. Reaction of $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$ (2) with Arenes

amt of 2	amt of arene	amt of acetonitrile	solvent	time/temp[e]	product (yield)
100 mg (0.30 mmol)	$1,2,4\text{-}C_6H_3Me_3$ (10 mL)	108 μL (2.1 mmol)		2 days/rt	**6** (71%)
100 mg (0.30 mmol)	$1,2,3,4\text{-}C_6H_2Me_4$ (10 mL)	108 μL (2.1 mmol)		2 days/rt	**7** (64%)
250 mg (0.74 mmol)	$1,3,5\text{-}C_6H_3Me_3$ (20 mL)	0.1 mL (1.9 mmol)		5 days/70–80 °C	**8** (41%)
100 mg (0.30 mmol)	$C_6H_5CH{=}CH_2$ (0.2 mL, 0.87 mmol)	1.0 mL (190 mmol)	THF (20 mL)	12 h/rt	**9** (57%)[a]
200 mg (0.59 mmol)	$1\text{-Me-}4\text{-}CH_2{=}CMeC_6H_4$ (5.2 g, 39 mmol)	60 μL (1.2 mmol)		42 h/rt	**10** (53%)[c]
100 mg (0.30 mmol)	$trans\text{-}C_6H_5CH{=}CHC_6H_5$ (210 mg, 1.14 mmol)	1.0 mL (19.0 mmol)	THF (20 mL)	12 h/rt	**11** (55%)[b]
100 mg (0.30 mmol)	$(C_6H_5)_3As$ (545 mg, 1.78 mmol)	93 μL (1.78 mmol)	THF (16 mL)	42 h/rt	**14** (61%)
100 mg (0.30 mmol)	$(2\text{-}MeC_6H_4)_3P$ (99 mg, 0.33 mmol)	62 μL (1.2 mmol)	THF (11 mL)	2 weeks/rt	**15**[d]

[a] After recrystallization from hexane at −30 °C. [b] 36% after recrystallization from hexane at −20 °C. [c] After recrystallization from isopentane at −78 °C. [d] Could not be separated from excess of tri-*o*-tolylphosphine. [e] rt = room temperature.

min the precipitated red-brown solid, $[RuCl_2(\eta^6\text{-}1\text{-Me-}4\text{-}CH_2{=}CMeC_6H_4)]_2$, was filtered off, washed with acetone, and dried in a vacuum. Yield: 106 mg (79%). ^1H NMR ($CDCl_3$) δ 5.77, 5.34 (AB q, 4 H, J = 6.2 Hz, C_6H_4), 5.50 (s, 1 H, =C*H*H), 5.40 (d, 1 H, J = 1.5 Hz, =CH*H*), 2.19 (m, 3 H, C=CMe), 2.15 (s, 3 H, C_6H_4*Me*); IR (cm^{-1}, KBr) 1635 [ν(C=C)], 290 [ν(RuCl)]. Anal. Calcd for $C_{10}H_{12}Cl_2Ru$: C, 39.5; H, 3.9; Cl, 23.35. Found: C, 40.0; H, 4.2; Cl, 22.7.

Preparation of $Ru(\eta^6\text{-}1\text{-Me-}4\text{-}CH_2{=}CMeC_6H_4)(O_2CMe)_2$. Silver acetate (115 mg, 0.68 mmol) was added to a stirred suspension of $[RuCl_2(\eta^6\text{-}1\text{-Me-}4\text{-}CH_2{=}CMeC_6H_4)]_2$ (100 mg, 0.16 mmol) in benzene (20 mL). The mixture was stirred for 16 h under argon with exclusion of light and filtered through Celite. The filtrate was evaporated to dryness to give a yellow-brown solid, which afforded yellow-brown hygroscopic crystals (50 mg, 43%) of the required product from CH_2Cl_2/hexane. ^1H NMR ($CDCl_3$) δ 6.03, 5.59 (AB q, 4 H, J = 5.7 Hz, C_6H_4), 5.52, 5.39 (each s, 1 H, $=CH_2$), 2.25, 2.21 (each s, 3 H, C=CMe, C_6H_4*Me*), 1.90 (s, 6 H, O_2CMe); IR (cm^{-1}, KBr) 1625 vs, 1580 ms, 1510 s [ν_{asym}(OCO)], 1470 vs, 1380 ms, 1360 vs, 1310 vs [ν_{sym}(OCO)].

Exchange Reactions of $[RuH(C_{10}H_8)(C_8H_{12})]PF_6$ (16) with Aromatic Hydrocarbons. (a) *p*-Xylene. A solution of **16** (350 mg, 0.72 mmol) in dichloromethane (10 mL) was treated with an excess of *p*-xylene (5 mL, 41 mmol) and the mixture was stirred for 22 h at 0 °C. The dark brown solution was evaporated to dryness under reduced pressure. The ^1H NMR spectrum of the residue in CD_2Cl_2 still showed a small peak at δ −6.7 due to unchanged **16** in addition to a new peak at δ −5.8 due to $[RuH(p\text{-}C_6H_4Me_2)(C_8H_{12})]PF_6$ and the characteristic AA′BB′ pattern at δ 7–8 due to free naphthalene. The solution was therefore treated with *p*-xylene (5 mL) and CH_2Cl_2 (5 mL), stirred for another 4 h at 0 °C, and evaporated to dryness. The ^1H NMR spectrum in CD_2Cl_2 showed peaks due to $[RuH(p\text{-}C_6H_4Me_2)(C_8H_{12})]PF_6$ at δ 6.0 (C_6H_4), 4.2 (s), 3.5 (s) (CH_2 of COD), and −5.8 (s, RuH), but there were many other peaks due to unidentified impurities. The solvent was pumped off and the brown-black residue, dissolved in THF (10 mL), was treated with deaerated 10% aqueous Na_2CO_3. After 1 h the color had changed to yellow-brown. The solvent was removed under reduced pressure and the residue was extracted with benzene-d_6 to give a yellow solution. Evaporation of solvent gave $Ru(\eta\text{-}p\text{-}C_6H_4Me_2)(C_8H_{12})$ as a bright yellow solid. ^1H NMR (C_6D_6) δ 4.64 (s, C_6H_4), 3.2 (s, =CH), 2.34 (s, CH_2), 1.69 (s, Me); mass spectrum, m/z 316 (M^+). Anal. Calcd for $C_{16}H_{22}Ru$: C, 60.95; H, 7.0. Found: C, 61.4; H, 6.7.

(b) Mesitylene. The reaction was carried out as described above with **16** (250 mg, 0.52 mmol) and mesitylene (4 mL) in CH_2Cl_2 (10 mL). After 28 h the brown-black mixture was evaporated to dryness under reduced pressure. The main product was $[RuH(\eta\text{-}C_6H_3Me_3)(C_8H_{12})]PF_6$, identified by its ^1H NMR spectrum in CD_2Cl_2: δ 5.88 (s, C_6H_3), 4.0 (m), 3.4 (m) (CH_2), 2.23 (s, Me), −6.06 (s, RuH). A small amount of unchanged **16** was still present (singlet at δ −6.75). The residue was dissolved in THF (20 mL) and stirred with 10% aqueous Na_2DCO_3 (10 mL) for 1 h. The mixture was evaporated to dryness and the residue was extracted with hexane (3 × 20 mL). The extract yielded $Ru(\eta\text{-}C_6H_3Me_3)(C_8H_{12})$ (130 mg, 76%) as a yellow solid. ^1H NMR (C_6D_6) 4.65 (s, C_6H_3), 3.09 (s, =CH), 2.35 (s, CH_2), 1.73 (s, Me). This was identical with that of the compound obtained by heating $[RuCl_2(\eta\text{-}C_6H_3Me_3)]_2$ and 1,5-cyclooctadiene with 2-propanol in the presence of anhydrous Na_2CO_3[19] or by the reaction of $Ru(\eta^6\text{-}1,3,5\text{-}C_8H_{10})(\eta^4\text{-}1,5\text{-}C_8H_{12})$ (**1**) with mesitylene under hydrogen.[20]

Table III. Hydrogenation of 1-Hexene Catalyzed by Arene–Ruthenium(0) Complexes[a]

run	catalyst precursor	$[CH_3CN]$/[catalyst]	$p(H_2)$, atm	t, h	products (%)
1	**2**	0	1	4	*n*-hexane (55)
2	**2**	3	1	2	*n*-hexane (100)
3	**2**	10	1	2	*n*-hexane (100)
4	**1**	0	1	2	*n*-hexane (15) 2-hexene (6)[b]
5	**3**	0	1	4[c]	
6	**3**	10	1	4	
7	**3**	0	20	10	*n*-hexane (100)
8	**17**	0	1	4	
9	**17**	10	1	4	
10	**17**	0	20	10	*n*-hexane (100)

[a] Catalyst precursor (0.13 mmol), 1-hexene (1 mL, 8 mmol), THF (3 mL); catalyst precursors, $Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})$ (**1**), $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$ (**2**), $Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_8H_{12})$ (**3**), $Ru(\eta^6\text{-}1\text{-Me-}4\text{-}Me_2CHC_6H_4)(\eta^4\text{-}C_8H_{12})$ (**17**). [b] Mixture of *Z* and *E* isomers. [c] After 48 h under similar conditions, *n*-hexane (17%) is formed.[20]

(c) Hexamethylbenzene. Reaction of **16** (250 mg, 0.52 mmol) with hexamethylbenzene (250–500 mg, 1.5–3.0 mmol) in CH_2Cl_2 (10 mL) for periods up to 7 h gave small amounts of $[RuH(\eta\text{-}C_6Me_6)(C_8H_{12})]PF_6$, identified by its ^1H NMR singlet at δ −6.20 (RuH), but most of the starting material remained unchanged; the C_6Me_6 resonance of the product could not be identified. After 18 h, the signals due to both hydrides were still present but were much weaker. In addition to the singlet at δ 2.19 due to free C_6Me_6, there was a sharp singlet at δ 2.15, tentatively assigned to $[Ru(\eta\text{-}C_6Me_6)_2]^{2+}$ (lit.[21] $[Ru(\eta\text{-}C_6Me_6)_2](BF_4)_2$ in DMSO-d_6 δ 2.09).

Kinetic Studies. General Procedure. A weighed amount of **2** (ca. 30 mg) was placed in a 5-mm NMR tube fitted with a serum cap and a needle to vacuum or argon supply. The appropriate volumes of solvent and arene were added from a syringe, together with ca. 0.5 equiv of hexamethyldisiloxane as internal reference, and the mixture was shaken until the solid had dissolved. The required amount of CD_3CN was then added from a syringe and the progress of the reaction was monitored by ^1H NMR spectroscopy, using a pulse delay of 10 s. For the reaction with C_6D_6, the extent of formation of $Ru(\eta^6\text{-}C_6D_6)(\eta^4\text{-}C_8H_{12})$ (**3**-d_6) and loss of **2** were estimated by integration of the diene CH_2 resonances of each compound. For other arenes in THF-d_8, the extent of reaction was determined by integration of the olefinic resonances of each component, because the CH_2 resonances overlapped with a THF resonance at δ 1.78.

Catalytic Hydrogenation Reactions. These were carried out in a 50-mL round-bottomed flask equipped with a magnetic stirring bar and a side-arm closed with a serum cap. This was connected with a gas-volumetric apparatus containing hydrogen and maintained at a pressure of ca. 1 atm. Reactions requiring

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Table IV. Hydrogenation of C=C and C=O Functions Catalyzed by $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$ (2) and by $Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_8H_{12})$ (3)[a]

substrate	catalyst precursor	$p(H_2)$, atm	t, h	products (%)
2-heptene	2	1	2	
	2	20	1	*n*-heptane (100)
	3	20	10	*n*-heptane (40)
2,4,4-trimethyl-1-pentene	2	1	2	
	2	20	1	2,4,4-trimethylpentane (55)
	3	20	10	2,4,4-trimethylpentane (80)
cycloheptene	2	1	2	
	2	20	1	cycloheptane (100)
	3	20	10	cycloheptane (80)
styrene	2	1	2	ethylbenzene (8)[b]
	3	1	4	
1,5-cyclooctadiene	2	1	48	cyclooctene (64), cyclooctane (36)
	2	20	2	cyclooctane (100)
	3	1	48	cyclooctene (8)
	3	20	10	cyclooctene (15), cyclooctane (8), 1,3-cyclooctadiene (2)
1,3-cyclooctadiene	2	1	48	cyclooctene (58) cyclooctane (42)
2,3-dimethylbutadiene	2	1	24	
	2	20	24	2,3-dimethyl-2-butene (65), 2,3-dimethylbutane (35)
1-hexyne	2	1	24	*c*
	2	20	4	1-hexene (5) *n*-hexane (95)
acetone	2	1	24	
	2	20	24	2-propanol (20)
butyraldehyde	2	20	24	1-butanol (8)
crotonaldehyde	2	20	16	butyraldehyde (20)

[a] Catalyst precursor (0.13 mmol), substrate (8 mmol), THF (3 mL); 2 used in presence of CH_3CN (1.3 mmol). [b] ^1H NMR spectrum of reaction mixture shows formation of $Ru(\eta^6\text{-}C_6H_5CH_2CH_3)(\eta^4\text{-}C_8H_{12})$ and $Ru(\eta^6\text{-}C_6H_5CH{=}CH_2)(\eta^4\text{-}C_8H_{12})$ (9) [c] No hydrogenation; 2 converted into mixture of 1,3,5- and 1,2,4-cyclotrimer complexes $Ru[\eta^6\text{-}C_6H_3(CH_2CH_2CH_2CH_3)_3](\eta^4\text{-}C_8H_{12})$.

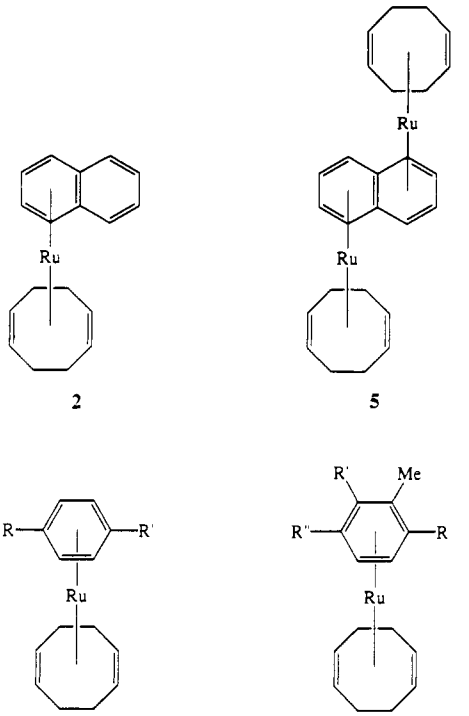
20 atm of hydrogen were done in a 125-mL stainless-steel rocking autoclave. In a typical experiment, a solution of **2** (50 mg, 0.15 mmol) in THF (3 mL) containing acetonitrile (26 μL, 0.5 mmol) under argon in a Schlenk tube was cooled to −78 °C. The vessel was evacuated and filled with hydrogen. The solution was transferred to the reaction flask, 1-hexene (1 mL, 8 mmol) was added from a syringe, and stirring was started. The reaction was stopped after 2 h. Analysis of the mixture by VPC showed >99% conversion into *n*-hexane. The results of these experiments are in Tables III and IV.

Results

Treatment of the bis(acetylacetonato) complex $Ru(acac)_2(\eta^4\text{-}1,5\text{-}C_8H_{12})$ with sodium naphthalide in THF gives $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}C_8H_{12})$ (**2**) as orange-brown crystals (eq 1 and Figure 1). Yields of 55–64% are ob-

$$Ru(acac)_2(C_8H_{12}) + 2NaC_{10}H_8 \rightarrow Ru(C_{10}H_8)(C_8H_{12}) + 2Na(acac) + C_{10}H_8 \quad (1)$$

tained after chromatography, high-vacuum sublimation to remove naphthalene, and crystallization from THF–hexane. Since hydrated $RuCl_3$ and 1,5-cyclooctadiene react to give $[RuCl_2(C_8H_{12})]_n$ almost quantitatively[17] and reaction of the latter with acetylacetone and Na_2CO_3 in DMF to give $Ru(acac)_2(C_8H_{12})$ proceeds in 80–85% yield, this procedure provides a convenient synthesis of **2** in gram quantities. The much lower yields of **2** obtained from $[RuCl_2(C_8H_{12})]_n$ and $LiC_{10}H_8$[13] are probably due to the insolubility of $[RuCl_2(C_8H_{12})]_n$ in the reaction medium. In agreement with earlier reports, the ^1H NMR spectrum of



4: R = H; R' = CN
9: R = H; R' = CH=CH$_2$
10: R = Me; R' = CMe=CH$_2$
11: R = H; R' = CH=CHPh
12: R = H; R' = AsPh$_2$
6: R = R'' = Me; R' = H
7: R = R' = R'' = Me
15: R = P(2-MeC$_6$H$_4$)$_2$; R' = R'' = H

Figure 1. New complexes of the type $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})$ prepared from $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$ (**2**).

2 shows a characteristic mirror-image pair of four-line patterns at δ 5.60 and 4.29 due to the protons of the coordinated ring of naphthalene (AA'BB' spin system) and a singlet at δ 7.11 due to the accidentally equivalent protons of the uncoordinated ring, in addition to the usual resonances arising from coordinated 1,5-cyclooctadiene. Correspondingly, the $^{13}C\{^1H\}$ NMR spectrum shows signals at δ 91.3 and 74.5 due to the carbon atoms of the coordinated ring of naphthalene and at δ 127.2 and 126.3 due to those in the uncoordinated ring.

Arene Exchange. In the absence of acetonitrile, **2** does not exchange with C_6D_6 at room temperature after 48 h, although some free naphthalene and 1,5-cyclooctadiene are formed owing to decomposition. Exchange does occur at ca. 50 °C, giving approximately equal amounts of $Ru(\eta\text{-}C_6D_6)(C_8H_{12})$ (**3**-d_6) and unchanged **2** after 4.5 h, but there is much decomposition. Neither THF nor acetone catalyze displacement of naphthalene; in fact, THF seems to inhibit it, because no replacement is observed after 4.5 h when **2** is heated with C_6D_6 at 50–60 °C in the presence of THF. In this respect, **2** differs from $M(\eta^6\text{-arene})(CO)_3$ (M = Cr, Mo, W), in which arene exchange is catalyzed by ketones and by THF,[22-24] and from $[Ir(\eta^6\text{-arene})(C_8H_{12})]^+$, in which arene exchange is promoted by acetone.[25,26]

As reported by Vitulli et al.,[9] displacement of naphthalene from **2** by various arenes is catalyzed by aceto-

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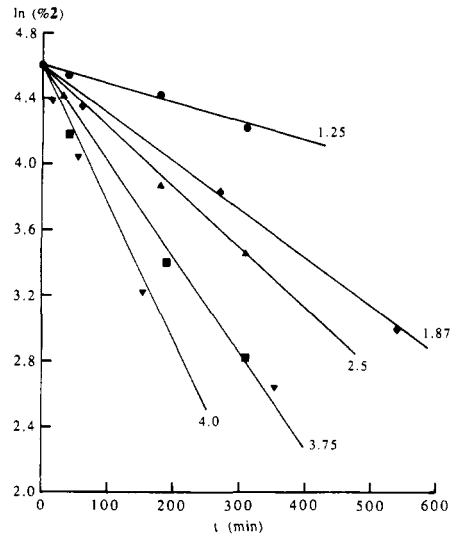
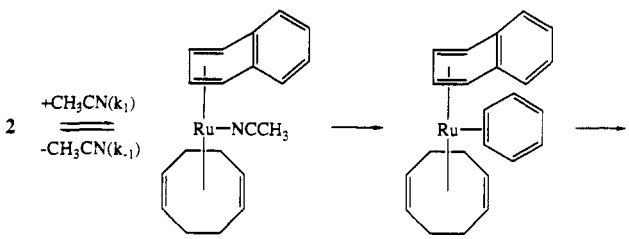


Figure 2. First-order plots for reaction of $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$ (**2**) with neat C_6D_6 in presence of various amounts of CH_3CN. Ratio [acetonitrile]/[2] = 1.25 (●), 1.87 (♦), 2.5 (▲), 3.75 (■), 4.0 (▼).

Scheme I. Acetonitrile-Catalyzed Displacement of Naphthalene from $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$ (2)



nitrile at room temperature. Exchange of benzene with $Ru(\eta^6\text{-}C_6H_6)(C_8H_{12})$ (**3**) at 50 °C is also catalyzed by acetronitrile,[25] but the process is clearly slower than in the case of **2**. Some preliminary information about the kinetics of replacement of naphthalene in **2** by C_6D_6 at 30 °C has been obtained. The extent of formation of **3**-d_6 at various times was determined by integrating the C_8H_{12} methylene proton signals of the product against the same proton signals in **2**. The procedure is not ideal because the chemical shifts are similar and the peaks are not sharp singlets, so the accuracy of the derived rate constants is probably not greater than 20%. Although known amounts of hexamethyldisiloxane were added as an internal reference in an attempt to determine the actual concentrations of each species, the results proved to be unreliable. For concentrations of acetonitrile up to ca. 4 mol per mol of **2**, reasonable first-order plots were obtained up to 5–10 half-lives (Figure 2). Although a plot of the derived rate constants against acetonitrile concentration is approximately linear up to [CH_3CN]/[2] ca. 3 (Figure 3), the data are not good enough to exclude a higher order dependence. The results are somewhat similar to those of Traylor et al.[24] for arene exchange with $Cr(C_6H_6)(CO)_3$ catalyzed by cyclohexanone and are consistent with initial formation of a reactive η^4-naphthalene complex that is stabilized by coordination of acetonitrile (Scheme I). At this stage, we cannot exclude the possibility that further intermediates of lower hapticity, e.g., one containing η^2-naphthalene and two acetonitrile ligands, are also involved.

Since benzonitrile and *n*-butyl cyanide are better catalysts than acetonitrile for arene exchange in $Cr(\eta^6\text{-arene})(CO)_3$,[22] we examined the efficacy of other nitriles in promoting the replacement of naphthalene in **2** by C_6D_6.

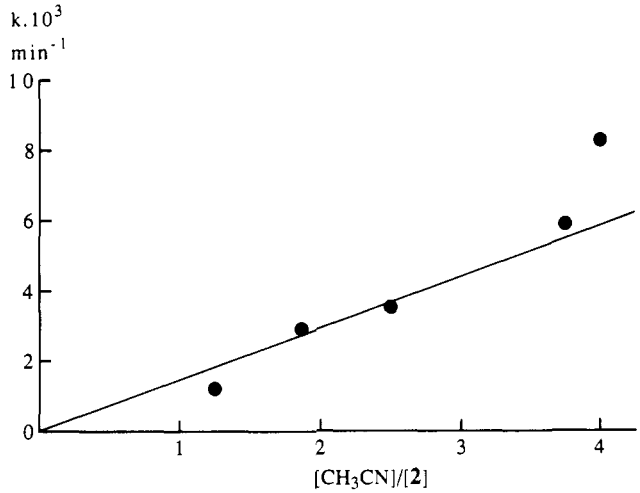


Figure 3. Plot of first-order rate constants for reaction of $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$ (**2**) with neat C_6D_6 versus the ratio [acetonitrile]/[2].

With *n*-propyl cyanide as catalyst, 47% of **3**-d_6 is formed after 60 min, whereas with acetonitrile it takes 93 min to form the same amount of **3**-d_6. However, the higher boiling point of *n*-propyl cyanide (115 °C) relative to that of acetonitrile (82 °C) makes *n*-propyl cyanide less convenient for the synthesis of thermally sensitive compounds. Addition of 6 mol of benzonitrile to a solution of **2** in C_6D_6 gives, after 50 min, free naphthalene and the η^6-benzonitrile complex $Ru(\eta^6\text{-}C_6H_5CN)(C_8H_{12})$ (**4**). This can be isolated as an air-stable yellow solid from reaction of benzonitrile with **2** in THF at room temperature over 2 days. Its ^1H NMR spectrum shows a characteristic set of resonances in a 2:2:1 ratio in the region δ 4–5 corresponding to the coordinated arene protons, in addition to the C_8H_{12} protons. There is no evidence for the formation of an N-bonded complex. After 5 days the mixture derived from **2** and benzonitrile in C_6D_6 contains about 30% of **4** and 70% of **3**-d_6 owing to slow exchange with the solvent, but there is also much decomposition. We conclude that acetonitrile is the most suitable catalyst for replacement of naphthalene from **2**.

Unfortunately, the catalyst acetonitrile or acetonitrile-d_3 is not a suitable solvent for carrying out or monitoring arene exchange reactions on **2** owing to precipitation of the insoluble red species $Ru_2(C_8H_{12})_2(C_{10}H_8)$ (**5**) (see below). A similar problem arises with acetone-d_6. Dichloromethane causes decomposition and cyclohexane is only partly miscible with acetonitrile. The solvent of choice is THF-d_8, which seems to give rise to less decomposition than the other solvents investigated; however, its signal at δ 1.73 overlaps with the resonance due to the CH_2 protons of **2**, so that the extent of replacement of naphthalene can only be determined by monitoring either the olefinic resonances (4 H) of coordinated 1,5-cyclooctadiene or the two 2 H resonances of the coordinated ring of naphthalene; we chose the former. In THF-d_8 containing 4 mol of CD_3CN per mol of **2** the rates of reaction of **2** with 10 mol and 30 mol of benzene are equal, within experimental error (3.3×10^{-4} min^{-1} and 4.1×10^{-4} min^{-1}, respectively); the rate of reaction with 3 mol of benzene is somewhat lower (1.6×10^{-4} min^{-1}). This result is consistent with the mechanism of Scheme I and with the results obtained for catalyzed arene exchange in $M(\eta^6\text{-arene})(CO)_3$[22-24] and $[Ir(\eta^6\text{-arene})(C_8H_{12})]^+$.[25,26]

Benzene, toluene, and xylene (10 mol per mol of **2**) react with **2** in THF-d_8 containing 4 mol of CD_3CN at essentially equal rates, although after 3 days a small difference in the

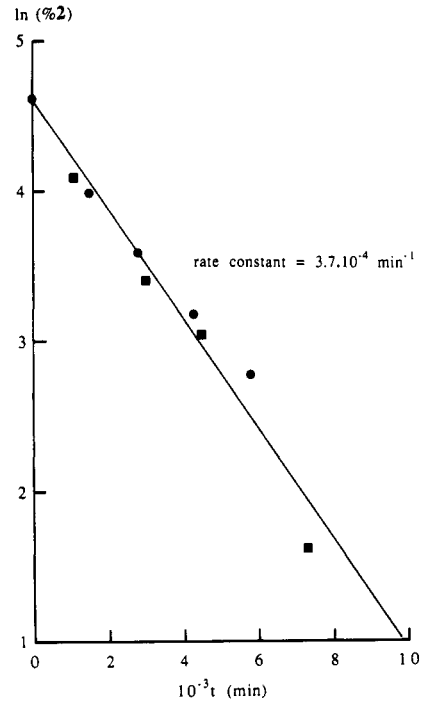


Figure 4. First-order plot for reaction of $Ru(\eta^6\text{-}C_{10}H_8)(\eta^6\text{-}C_8H_{12})$ (**2**) with an excess of *p*-xylene in the presence of acetronitrile (4 mol per mol of **2**) in THF-d_8. Plot combines data from separate runs in which 8 mol and 10 mol of *p*-xylene per mol of **2** were present initially. The appropriate points are marked as ■ and ●, respectively.

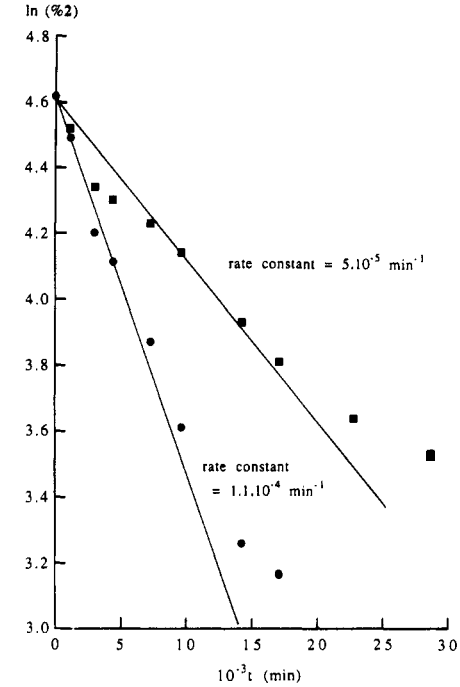


Figure 5. First-order plots for reactions of $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$ (**2**) with 1,2,4-trimethylbenzene (8 mol per mol of **2**) (●) and with 1,2,3,4-tetramethylbenzene (8 mol per mol of **2**) (■) in the presence of acetonitrile (4 mol per mol of **2**) in THF-d_8.

extent of formation of $Ru(\eta^6\text{-arene})(C_8H_{12})$ is evident, the order being xylene > toluene > benzene. Figure 4 shows the first-order plot for the reaction of **2** with an excess of *p*-xylene in THF-d_8. When there are more than two methyl groups in the arene ring, steric effects become important. Mesitylene (1,3,5-trimethylbenzene) does not react with **2** under the conditions described above after 1 week; after 6 h at 50 °C, 5–10% of product can be detected, but there is much decomposition and other unidentified products are present. In contrast, 1,2,4-trimethylbenzene (8 mol) cleanly displaces naphthalene from **2** under the usual conditions (Figure 5), the first-order rate constant (1.1×10^{-4} min^{-1}) being significantly less than that for *p*-xylene (3.7×10^{-4} min^{-1}). Displacement by 1,2,3,4-tetramethylbenzene is slower still ($k = 5 \times 10^{-5}$ min^{-1}). These results are in interesting contrast to those obtained for the closely related cationic complex $[Ir(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})]^+$,[25,26] in which the rate of arene exchange is independent of the degree of methyl substitution for *three* or fewer methyl groups.

When **2** is dissolved in 1,2,4-trimethylbenzene or 1,2,3,4-tetramethylbenzene in the presence of acetonitrile (ca. 7 mol), reaction is complete within 2 days at room temperature and the $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})$ complexes (arene = 1,2,4-$C_6H_3Me_3$ (**6**), 1,2,3,4-$C_6H_2Me_4$ (**7**)) can be isolated as stable, yellow solids in 60–70% yield. The corresponding mesitylene complex **8** can be obtained in an impure state in ca. 40% yield after 5 days at 70–80 °C. Similar compounds (**9**–**11**) have been obtained by reaction of **2** with styrene, *p*-isoprenyltoluene, and *trans*-stilbene, respectively (Table II). The ^{1}H NMR spectra of **9**–**11**, especially the characteristic shielding of the aromatic protons, show that the $Ru(C_8H_{12})$ unit is bound to the arene and that the double bonds are free. Preliminary experiments indicate that the attachment of a second $Ru(C_8H_{12})$ unit to the uncoordinated ring of $Ru(\eta^6\text{-}PhCH{=}CHPh)(C_8H_{12})$ (**11**) requires ca. 5 days. Treatment of **10** in acetone with HCl gives the η^6-arene–ruthenium(II) complex $[RuCl_2(\eta^6\text{-1-Me-4-}CH_2{=}CMeC_6H_4)]_2$ (**12**) as a poorly soluble red-brown solid; this can be converted into the more soluble, monomeric bis(acetato) complex $Ru(O_2CMe)_2(\eta^6\text{-1-Me-4-}CH_2{=}CMeC_6H_4)$ (**13**) by treatment with silver acetate (2 mol). Both compounds show a pair of doublets due to the coordinated arene protons and two singlets due to the uncoordinated olefinic protons in the region δ 5–6. The IR spectrum of **13** contains strong bands assignable to both unidentate and bidentate acetate groups in the region 1625–1310 cm^{-1}, similar to those reported for other η^6-arene complexes $Ru(\eta^2\text{-}O_2CMe)(\eta^1\text{-}O_2CMe)(\eta^6\text{-arene})$.[27] The acetate methyl groups appear as a singlet at δ 1.90, probably owing to rapid exchange of the unidentate and bidentate functions.

It is worth noting that reaction of $Ru(\eta^6\text{-1,3,5-}C_8H_{10})(\eta^4\text{-1,5-}C_8H_{12})$ (**1**) with styrene under hydrogen gives a mixture of the η^6-styrene complex **9** and the η^6-ethylbenzene complex $Ru(\eta^6\text{-}C_6H_5CH_2CH_3)(C_8H_{12})$.[28] Also, attempts to make **12** by reaction of 2-methyl-5-isoprenyl-1,3-cyclohexadiene with ethanolic $RuCl_3$ have given only intractable black solids. Clearly the naphthalene complex **2** is the most convenient precursor for ruthenium complexes of arenes having olefinic substituents.

In the presence of acetonitrile, **2** reacts with triphenylarsine to give the yellow η^6-arene complex $Ru(\eta^6\text{-}C_6H_5AsPh_2)(\eta^4\text{-}C_8H_{12})$ (**14**), isolated in ca. 60% yield. This shows a 2:2:1 pattern of resonances in the region δ 4.0–5.5, characteristic of a η^6-coordinated phenyl ring. Similarly, the bulky ligand tri-*o*-tolylphosphine reacts with **2** to give $Ru\{\eta^6\text{-2-}MeC_6H_4P(C_6H_4Me\text{-2})_2\}(\eta^4\text{-}C_8H_{12})$ (**15**), which could not be separated from the free ligand but was identified by its NMR (^{1}H, ^{31}P) spectra and mass spectrum (Table I). There was no evidence for the formation of conventional group 15–donor complexes with either triphenyl-

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arsine or tri-o-tolylphosphine. The behavior of **2** with these ligands is somewhat similar to that of the group 6 carbonyls; e.g., triphenylarsine reacts directly with $Cr(CO)_6$ to give the η^6-arene complex $Cr(\eta^6\text{-}C_6H_5AsPh_2)(CO)_3$, although the As-donor complex $Cr(CO)_5(AsPh_3)$ can be obtained by reaction of $AsPh_3$ with $[CrCl(CO)_5]^-$ in the presence of a Lewis acid.[29] Likewise, tri-o-tolylphosphine reacts with $M(CO)_6$ (M = Cr, Mo) to give η^6-arene complexes $M(CO)_3\{\eta^6\text{-}2\text{-}MeC_6H_4P(C_6H_4Me\text{-}2)_2\}$.[30] Reactions of **2** with other group 15 ligands are under investigation.

Attempts to characterize $Ru(C_8H_{12})$ complexes containing π-bonded heterocycles have not been successful so far. At room temperature over 4 days **2** reacts with neat 2,6-dimethylpyridine in the presence of acetonitrile to give a small amount of a solid that contains at least two $Ru(C_8H_{12})$ species, according to the ^1H NMR spectrum. The presence of signals in the region δ 4.7–5.3 suggests that one of these compounds is $Ru(\eta^6\text{-}2,6\text{-}Me_2C_5H_3N)(C_8H_{12})$, but there are also resonances at δ 6.0–6.2 suggestive of a conventional N-donor complex, possibly $Ru(C_8H_{12})(2,6\text{-}Me_2C_5H_3N)_3$. There was no reaction observable by ^1H NMR spectroscopy between **2** and 2,6-di-*tert*-butylpyridine in THF-d_8 and CD_3CN (4 mol).

Formation of the Dinuclear Complex $Ru_2(C_8H_{12})_2(C_{10}H_8)$ (5). At intermediate stages of the reaction of **2** with C_6D_6 in the presence of acetonitrile, a pair of mirror-image multiplets at δ 5.5 and 4.1 was observed, whose intensity was about 10% of the peaks due to **2** at δ 5.60 and 4.29. When an excess of acetonitrile (ca. 10 mol) is added to a solution of **2** in acetone-d_6, red-brown microcrystals precipitate. This solid also precipitates during the early stages of many of the acetonitrile-catalyzed naphthalene displacement reactions discussed above, but it redissolves as the reactions proceed. Microanalysis shows that nitrogen is absent and is consistent with the formula $Ru_2(C_8H_{12})_2(C_{10}H_8)$ (**5**). The mass spectrum shows a parent ion peak at 547.9 together with a peak at 338 due to $Ru(C_{10}H_8)(C_8H_{12})$. The IR spectrum does not contain any band assignable to ν(CN) of acetonitrile, although samples made in acetone do have a weak peak at 1712 cm^{-1}, possibly due to the presence of small amounts of acetone in the lattice. In solution, **5** slowly forms **2** and free 1,5-cyclooctadiene. Thus, if C_6D_6 is added to **5** and the ^1H NMR spectrum is recorded immediately, the characteristic pair of multiplets at δ 5.45 and 4.01 is observed together with the corresponding pair for **2** (ca. one-third the intensity). Integration suggests that the C_8H_{12} protons of **2** and **5** are coincident. After 4 h the resonances due to **5** have disappeared and those due to $Ru(C_6D_6)(C_8H_{12})$ (**3**-d_6) have grown. Similarly, the ^1H NMR spectrum of **5** in THF-d_8, recorded immediately after dissolution, shows the presence of **2** and **5** in ca. 2:1 ratio: after 2 h, **5** has disappeared and only **2**, free 1,5-cyclooctadiene, and free naphthalene (formed by decomposition) are present. **5** clearly acts as a source of the very reactive 12e fragment $Ru(C_8H_{12})$, which can be stabilized to some extent by coordination of THF or acetonitrile (eq 2). Unfortunately, we have been unable to grow crystals

$$Ru_2(C_8H_{12})_2(C_{10}H_8) \rightleftarrows Ru(C_{10}H_8)(C_8H_{12}) + Ru(C_8H_{12})(solvent)_n \quad (2)$$

of **5** suitable for X-ray structural analysis, but it seems likely that η^6,η^6-naphthalene bridges two transoid $Ru(C_8H_{12})$ units; this arrangement has been found in the isoelectronic bis(η^6-benzene)dichromium complex $Cr_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}\eta^6,\eta^6\text{-}C_{10}H_8)$.[7] The ^1H NMR spectrum of **5** seems to exclude the possibility that both $Ru(C_8H_{12})$ units are bound to the same ring, although dinuclear complexes of vanadium,[31] chromium,[32] iron,[33] and cobalt[33] that contain bridging monocyclic arenes are known. The formation of **5** from **2** can be compared with the much slower decomposition of $Cr(\eta^6\text{-}C_{10}H_8)_2$ to $Cr_n(\eta^6,\eta^6\text{-}C_{10}H_8)_n$.[34]

Protonation of $Ru(C_{10}H_8)(C_8H_{12})$. The ruthenium(II) complex $[RuCl_2(\eta^6\text{-}C_{10}H_8)]_2$ would obviously be a useful synthetic precursor, but unfortunately attempts to make it by treatment of **2** with HCl gave only free naphthalene and unidentified decomposition products. However, treatment of a solution of **2** in ether with aqueous HPF_6 gives the pale yellow monoprotonated ruthenium(II) salt $[RuH(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})]PF_6$ (**16**) in 70–80% yield. The IR spectrum contains a very weak absorption at 2050 cm^{-1} assigned to ν(RuH), in addition to characteristic bands due to PF_6^-, and the ^1H NMR spectrum shows a singlet hydride resonance at δ −6.7. There are also two 2 H multiplets due to the coordinated diene protons at δ 4.31 and 3.95, four 2 H multiplets due to the diene methylene protons in the region δ 1.3–2.3, a sharp singlet at δ 6.33 due to the accidentally isochronous protons of the coordinated ring of naphthalene, and a complex doublet at δ 7.9 arising from the corresponding uncoordinated ring protons. Similar spectra have been recorded for other $[RuH(\eta^6\text{-arene})(\eta^4\text{-}1,5\text{-}C_8H_{12})]^+$ complexes, though there is evidence from deuteration studies that an isomeric, agostic η^3-cyclooctenyl complex or a hydrido(1,3-cyclooctadiene) complex is present in equilibrium with the hydrido(1,5-cyclooctadiene) species.[35] The reduction in symmetry caused by protonation at the metal atom is evident in the doubling of the olefinic and methylene signals of $1,5\text{-}C_8H_{12}$ in the ^1H NMR spectrum and in the appearance of two resonances at δ 80.2 and 74.9 due to the olefinic carbon atoms in the $^{13}C\{^1H\}$ NMR spectrum. The ^1H and ^{13}C resonances of the coordinated ring of naphthalene in **16** are less shielded than those in **2**, suggesting that the naphthalene is bound fairly weakly. Indeed, solutions of **2** in CH_2Cl_2 decompose with loss of naphthalene over about a day, even in the absence of air, and react with benzene, *p*-xylene, or mesitylene to give the salts $[RuH(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})]PF_6$, together with unidentified decomposition products. These compounds have been identified by their ^1H NMR spectra, by comparison with authentic materials, and by conversion into $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})$ on reaction with aqueous Na_2CO_3. **16** also reacts slowly with an excess of hexamethylbenzene to give small amounts of $[RuH(\eta\text{-}C_6Me_6)(C_8H_{12})]PF_6$, but this seems to undergo further reactions to give $[Ru(\eta\text{-}C_6Me_6)_2]^{2+}$, among other products.

Catalytic Hydrogenation. The lability of the naphthalene–ruthenium bond suggests that $Ru(C_{10}H_8)(C_8H_{12})$ (**2**) could be a useful precursor for homogeneous catalysis. There are few examples of non-carbonyl-containing Ru(0) complexes acting as homogeneous hydrogenation catalysts: $Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})$ (**1**) catalyzes the hydrogenation of cycloheptatriene to cycloheptene[36] and $Ru(\eta^6\text{-arene})(\eta^4\text{-}$

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C_8H_{12}) complexes (arene = benzene, *p*-xylene, or mesitylene) catalyze olefin hydrogenation at hydrogen pressures of 1–20 atm.[20] Also, $Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)$ is reported to catalyze hydrogenation of benzene and other aromatic compounds to the corresponding cyclohexanes.[37]

Complex **2** catalyzes homogeneously the hydrogenation of 1-hexene to *n*-hexane at room temperature and atmospheric pressure. Its efficiency in this reaction is compared with that of $Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})$ (**1**), $Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_8H_{12})$ (**3**), and $Ru(\eta^6\text{-1-Me-4-Me}_2\text{CHC}_6H_4)(\eta^4\text{-}C_8H_{12})$ (**17**) in Table III. Complex **2** is clearly more active than **3** or **17**, since these do not catalyze hydrogenation of 1-hexene under ambient conditions, although they will do so under 20 atm of H_2. As expected, acetonitrile enhances the activity of **2** under ambient conditions (compare runs 1 and 2 or 3 in Table IV) but does not improve the activity of **3** or **17**. Complex **1** also catalyzes hydrogenation of 1-hexene, but it is less active than **2** and there is some competing isomerization to (*E*)- and (*Z*)-2-hexene.

The results of other catalytic hydrogenations are summarized in Table IV. In the presence of acetonitrile, **2** catalyzes hydrogenation of the sterically hindered terminal olefin 2,4,4-trimethyl-1-pentene and of the internal olefins 2-heptene and cycloheptene to the corresponding alkanes, although it is necessary to use 20 atm of hydrogen. 1,5-Cyclooctadiene is slowly hydrogenated to a mixture of cyclooctene and cyclooctane at 1 atm of hydrogen in the presence of **2** and is completely hydrogenated to cyclooctane under 20 atm of hydrogen. 2,3-Dimethylbutadiene is unaffected under 1 atm of H_2, but is slowly hydrogenated to a mixture of 2,3-dimethyl-2-butene and 2,3-dimethylbutane under 20 atm of H_2. Styrene is hydrogenated to a small extent to ethylbenzene at 1 atm, but the catalyst is converted into a mixture of $Ru(\eta^6\text{-styrene})(\eta^4\text{-}C_8H_{12})$ and $Ru(\eta^6\text{-ethylbenzene})(\eta^4\text{-}C_8H_{12})$ under the reaction conditions. 1-Hexyne also shows little hydrogenation, even under 20 atm of H_2, probably because of rapid cyclotrimerization of the alkyne in the presence of **2**. Slow hydrogenation of the carbonyl groups of acetone and 1-butanal, and of the olefinic double bond of crotonaldehyde, is observed. In all cases studied, the η^6-benzene complex **3** is either catalytically inactive or much less active than **2** under the same conditions.

At the end of the catalytic hydrogenations the solutions are clear and do not contain suspended solids. In the case of **2** as precursor, the final species present are probably ruthenium(0) complexes stabilized by coordination of acetronitrile. Compounds of this type have been proposed as the active catalysts in the isomerization of olefins catalyzed by **2**.[38]

Discussion

All previous preparations of naphthalene complexes of ruthenium(0) or ruthenium(II) have employed the neutral ligands, not their derived anions.[21,39,40] Sodium naphthalide has been used to make η^4- and η^6-naphthalene complexes of early transition elements, e.g., $TaCl(\eta^4\text{-}C_{10}H_8)(Me_2PCH_2CH_2PMe_2)$[41] and $Ti(\eta^6\text{-}C_{10}H_8)\{t\text{-BuSi}(CH_2PMe_2)_3\}$.[42] The most closely related application in the case of ruthenium seems to be the reduction of *cis*-$RuCl_2(Me_2PCH_2CH_2PMe_2)_2$ to give the *cis*-hydrido(2-naphthyl)ruthenium(II) complex $RuH(C_{10}H_7)(Me_2PCH_2CH_2PMe_2)_2$, which is believed to be in tautomeric equilibrium with a $(\eta^2$-naphthalene)ruthenium(0) complex $Ru(\eta^2\text{-}C_{10}H_8)(Me_2PCH_2CH_2PMe_2)_2$.[43]

The single-crystal X-ray analysis of **2**[13,15] confirms that the naphthalene is hexa*hapto*; it shows, however, a slip distortion toward η^4 bonding, the carbon atoms of the ring junction being further from, and presumably more weakly bonded to, the ruthenium atom than are the remaining carbon atoms of the coordinated six-membered ring. Further evidence for the tendency toward η^4-bonding is the fact that the coordinated ring is bent by about 8° along the vector joining the carbon atoms adjacent to those of the ring junction. This ground-state weakening of the metal–arene bond undoubtedly contributes to the lability of the naphthalene ring. Of the solvents investigated, only alkane nitriles, especially acetonitrile, seem to be capable of stabilizing the η^4- or η^2-naphthalene intermediates that are implicated in ligand substitution and catalytic hydrogenation; O-donor solvents such as acetone and THF are ineffective. In contrast, acetone labilizes the coordinated arene in $[Ir(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})]^+$,[25,26] presumably owing to a strong electrostatic interaction between the positive charge on the metal atom and the oxygen atom of the solvent. The fact that O-donor solvents also labilize naphthalene in $Cr(\eta^6\text{-}C_{10}H_8)(CO)_3$[2,3] is presumably a consequence of a similar effect arising from a positive charge on the metal atom induced by the strongly π-accepting CO ligands.

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